$$ {}_{11}\mathrm{Na}^{23}+{}_{1}\mathrm{D}^{2}+(\text{k.e. of } \mathrm{D}^{2}) = \mathrm{Na}^{24}+\mathrm{H}^{1}+(\text{k.e. of } \mathrm{H}^{1})+(\text{k.e. of } \mathrm{Na}^{24}). $$

Using the chemical value for Na^{23}, and the observed maximum proton energy, 6.2 mv (=0.0067 mass unit), we obtain

$$ {}_{11}\mathrm{Na}^{24}=22.999\pm0.003+2.0136+0.0023-1.0078-0.0067-0.0006 =24.000\pm0.003. $$

Finally if the difference in mass between Na^{24} and Mg^{24} is represented by the sum of the maximum energy of the beta-rays (1.2 mv) and the energy of the gamma-rays, 5.5±0.5 mv, we have

$$ \mathrm{Mg}^{24}=24.000\pm0.003-0.0013-0.0059 =23.993\pm0.003. $$

It should be noted that the assumed relation between the maximum energy of the beta-particles and the mass change in the beta-disintegration has not heretofore been established by experiment or justified by theory. The fact that the value for the mass of Mg^{24} obtained in this way fits satisfactorily on Aston's mass defect curve therefore may be interpreted as experimental evidence favoring the validity of this fundamental assumption.

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Comparison of the Spectra of CaH and CaD

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The spectrum of calcium deuteride has been photographed at high dispersion with a Ca arc in an atmosphere of heavy hydrogen as a source. Quantum analyses of the B and C systems are presented, and the rotational energy constants and spin doubling of the two states of the B bands are compared with those for CaH. The ratio B_e^i/B_e for the ground state is 0.51337 whereas the ratio of the reduced masses is 0.51276. This represents a decrease of 0.059 percent for the equilibrium internuclear distance in CaD. The spin doubling in the $B\,{}^2\Sigma$ state of CaD does not show the irregular variation with K found in CaH, and is of magnitude almost exactly in the ratio ρ^2 with that of the Λ-doubling in the $A\,{}^2\Pi$ state of CaH. Multiple large perturbations occurring in the $C\,{}^2\Sigma$ state of CaD are described.

INTRODUCTION

In the several band systems of the CaH molecule are to be found striking examples of the phenomena of l-uncoupling, Λ-doubling, predissociation and perturbations.[1] The magnitudes of all of these effects depend upon the rotational constants B_v and the relative spacing of the rotational energy levels in the interacting states. Substitution of deuterium for hydrogen in this molecule therefore produces, because of the relatively large change in the reduced mass, interesting variations in these phenomena. In addition, the study of the hydrogen isotope effect in these bands provides an example for the prediction by Kronig[2] that in certain cases the potential energy function for the vibration of the non-rotating molecule is not identical for the two isotopes, the equilibrium distance being slightly smaller for the heavier isotope.

EXPERIMENTAL PROCEDURE

The light source was a d.c. arc carrying 2.5 amperes between a water-cooled copper anode and a hollow copper cathode filled with metallic

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[1] For references cf. W. Jevons, *Report on Band-Spectra of Diatomic Molecules.*

[2] R. de L. Kronig, Physica 1, 617 (1934).

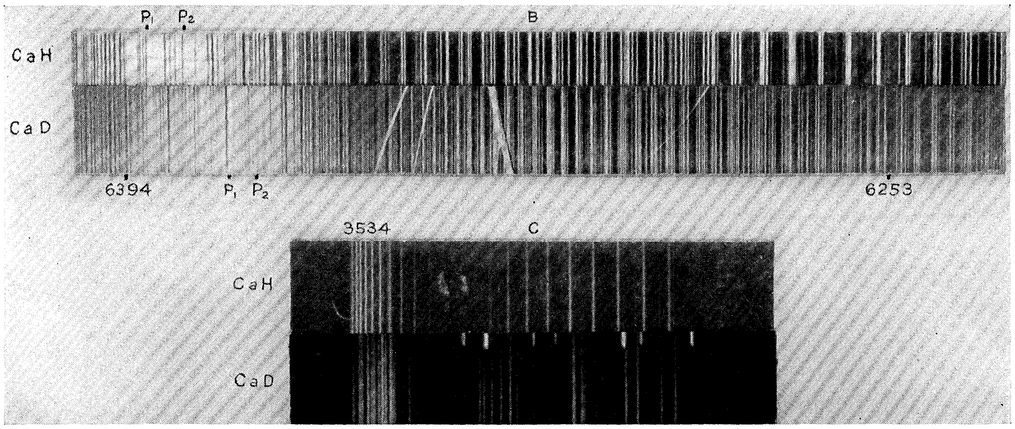

FIG. 1. Spectrograms of the B and C bands of CaH and CaD. Both of the CaD spectra have the CaH bands present with low intensity, and the spectrogram of the CaH C band shows some of the CaD lines. Note the marked difference between the C bands of the two isotopes.

calcium in an atmosphere of heavy hydrogen at about 4 cm of Hg pressure. The heavy hydrogen was obtained from a gram of 98 percent heavy water by interaction with calcium metal in a vacuum. Only half of the deuterium in the heavy water was liberated, of course, but the CaOD formed in the reaction was desired as a target containing deutons for a nuclear disintegration experiment in this laboratory. From the storage flask of about one liter capacity, heavy hydrogen was admitted occasionally during an exposure to the arc chamber, which had a volume of about two liters, in order to replenish the gas consumed in the manufacture of CaD_2.

Spectrograms of the A, B and C band systems of CaD were obtained in the second order of a 21-foot concave grating in a stigmatic mounting, the dispersion being about 2.2A/mm. Eastman Hypersensitive Panchromatic, I–S and Eastman 40 plates were used for the B, A and C band regions, respectively. That the light source was intense may be judged from the fact that the exposure times were in all cases about 15 minutes. On all the spectrograms CaH spectra are present, ordinary hydrogen having come from the walls and the hot electrodes, but the band lines due to CaD are several times more intense than the corresponding CaH lines.

Since there is but slight difference in the vibrational frequencies of the CaH molecule in the two states involved in each of these band systems, the $\Delta v=0$ sequence is very much stronger than the other sequences. Therefore according to the simple theory of the vibrational isotope effect the corresponding $\Delta v=0$ sequences of the CaD bands should be but little displaced from those of CaH. The resulting overlapping and interlacing of the rotational structure of the bands of the two isotopic molecules is troublesome, but the relative simplicity of the B and C bands (both $^2\Sigma\rightarrow{}^2\Sigma$) together with the greater intensity of the CaD lines makes the quantum analysis possible. The structure of the A band ($^2\Pi\rightarrow{}^2\Sigma$) of CaD at 7000A, however, is so complicated by the numerous fusions of lines with those of the weaker CaH bands as to defy accurate quantum analysis. At this time therefore a discussion only of the B and C band systems of CaD is presented. In Fig. 1 are displayed reproductions of typical spectrograms of these bands.

THE B BANDS OF CaD

The $\Delta v=0$ sequence of this system lies mostly in the region 6200 to 6400A, the origin of the 0,0 band falling within a few wave numbers of that of the corresponding CaH band. Since the reduced mass of CaD is almost twice that for CaH, the rotational energy levels of the former will have but half the spacing of the CaH levels. There will thus be roughly twice as many lines

TABLE I. *Assignment of frequencies in the "B" $^2\Sigma \rightarrow {}^2\Sigma$ 0,0 and 1,1 bands of CaD. cm^{-1} units.*

$J''+\frac{1}{2}$	0,0				1,1			
	P_1	R_1	P_2	R_2	P_1	R_1	P_2	R_2
1				15758.62		15739.40		15744.53
2	15744.52	15757.47	15740.73	63.71	15730.98	43.88	15727.48	49.32
3	40.09	62.20	37.05	68.96	26.55	48.25	23.39	54.21
4	35.86	67.11	33.40	74.35	22.42	52.74	19.53	59.31
5	31.80	72.12	29.82	79.92	18.31	57.33	15.85	64.57
6	27.94	77.17	26.59	85.58	14.28	62.33	12.61	69.95
7	24.17	82.50	23.43	91.50	10.38	67.14	09.01	75.47
8	20.56	87.90	20.56	97.43	06.70	72.31	06.00	81.15
9	17.35	93.52	17.74	803.56	02.95	77.64	03.05	86.99
10	14.15	99.16	15.12	09.92	699.56	83.30	00.21	92.85
11	11.05	805.12	12.61	16.32	96.48	88.76	697.78	99.10
12	08.24	11.16	10.35	22.88	93.72	94.25	95.47	805.10
13	05.56	17.29	08.24	29.63	91.24	99.90	93.03	11.47
14	02.92	23.64	06.29	36.56	87.97	805.88	90.79	18.09
15	00.28	30.02	04.51	43.20	85.22	11.94	88.76	24.39
16	698.53	36.56	02.92	50.48	83.07	18.09	87.07	31.21
17	96.49	43.20	01.46	57.69	81.15	24.39	85.22	37.98
18	94.58	50.10	00.28	64.99	78.69	30.69	83.87	44.89
19	92.92	57.06	699.00	72.45	76.93	37.25	82.65	51.85
20	91.42	64.09	98.07	79.98	75.29	43.86	81.22	58.90
21	90.10	71.15	97.21	87.62	73.53	50.56	80.51	66.13
22	88.80	78.52	96.49	95.38	72.39	57.27	79.66	73.34
23	87.69	85.85	96.13	903.16	71.19	64.18	78.69	80.69
24	86.82	93.32	95.76	11.11	69.70	71.23	78.23	88.12
25	86.20	900.81	95.54	19.15	69.01	78.18	77.64	95.47
26	85.64	08.51	95.54	27.18	68.30	85.25	77.39	903.14
27	85.15	16.16	95.76	35.34		92.43	76.93	10.65
28	84.93	23.96	96.13	43.53		99.69		18.36
29	84.76	32.01	96.49	51.83		906.97		26.03
30	84.76	39.74	97.00	60.13		14.26		33.76
31	85.15	47.72	97.74	68.50		21.67		41.51
32	85.64	55.75	98.53	76.98		29.05		49.31
33	86.20	63.80	99.46	85.18		36.49		57.02
34	86.74	71.91	700.62	93.86		43.96		64.92
35	87.61	80.02	02.03	16002.41		51.37		72.70
36	88.68	88.26	03.41	10.89		58.88		80.50
37	89.60	96.36	05.06	19.35		66.38		88.24
38	90.78	16004.58	06.70	27.94		73.82		96.05
39	91.93	12.82	08.24	36.51		81.29		16003.85
40	93.62	21.02	09.98	44.96		88.72		11.58
41	94.96	29.22		53.53		96.05		19.34
42	96.53	37.56		61.92		16003.43		26.81

in a given energy range in a branch of the deutride band. For example, the line R_1 ($55\frac{1}{2}$) of the CaD is close to R_1 ($30\frac{1}{2}$) of CaH. In the P-branches which form heads at about $K=26$ this closer spacing of the lines results in more fusions of lines at and near the heads, with resulting lessened accuracy of measurement. Table I contains the quantum assignments of frequencies in the 0,0 and 1,1 CaD bands, while in Table II are given the usual R–P combination differences from which the rotational energy constants are computed.

From the $\Delta_2F(K)$ values of Table II the constants B_v and D_v of the expression for the rotational energy of the molecule may be computed in the usual manner. Knowing B_0 and B_1, the quantities α and B_e of the relation $B_v=B_e-\alpha(v+\frac{1}{2})$ are obtained. B_e is the value of this rotational constant when the nuclei are at their equilibrium distance apart, and it is the ratio of these B_e constants for the same electronic state of the two isotopic molecules which should equal, according to the simple theory of the isotope effect in band spectra, the ratio of their reduced masses. It is important to note that the B_v values so calculated are really $B_v{}^*$ values,[3] differing considerably from the real B_v values for a state such as this upper $^2\Sigma$ state which interacts strongly with a near-lying $^2\Pi$ state. We return to this point below. In Table III are collected the results of these calculations, including revised and more accurate values for the corresponding constants of the CaH states.

For comparison of these constants for the two isotopes one needs the ratio ρ^2 of their reduced masses. Taking the mass-spectrograph determinations of 1.00778 and 2.01363 atomic weight units for hydrogen and deuterium,[4] respectively, and with $m_{\mathrm{Ca}}=39.97$, $\rho^2=\mu_{\mathrm{CaH}}/\mu_{\mathrm{CaD}}=0.51276$. Any possible departure of the mass of Ca from this value 39.97 affects ρ^2 inappreciably. From this value of ρ^2 it follows that $\rho=0.716066$, $\rho^3=0.367168$ and $\rho^4=0.262918$.

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[3] R. S. Mulliken and A. Christy, Phys. Rev. **38**, 87 (1931).

[4] K. T. Bainbridge, Phys. Rev. **41**, 115 (1932).

TABLE II. *Combination differences for the "B" $^2\Sigma\rightarrow{}^2\Sigma$ CaD band. The $\Delta_2F(K)$ values are the average of the R_1-P_1 and R_2-P_2 differences in each case.*

	Lower state combinations					Upper state combinations				
	0,0				1,1	0,0				1,1
$J''+\frac{1}{2}$	$R_1(J-1)$ $-P_1(J+1)$	$R_2(J-1)$ $-P_2(J+1)$	K''	$\Delta_2F''(K)$	$\Delta_2F''(K)$	$R_1(J)$ $-P_1(J)$	$R_2(J)$ $-P_2(J)$	K'	$\Delta_2F'(K)$	$\Delta_2F'(K)$
2		21.57					22.98			
3	21.61	30.31	2	21.59	21.30	22.11	31.91	2	22.54	21.77
4	30.40	39.14	3	30.36	29.87	31.25	40.95	3	31.58	30.57
5	39.17	47.76	4	39.15	38.41	40.32	50.10	4	40.63	39.40
6	47.95	56.49	5	47.86	46.83	49.23	58.99	5	49.66	48.38
7	56.61	65.02	6	56.55	55.59	58.33	68.07	6	58.66	57.04
8	65.15	73.76	7	65.09	64.07	67.34	76.87	7	67.70	66.03
9	73.75	82.31	8	73.76	72.58	76.17	85.82	8	76.52	74.92
10	82.47	90.95	9	82.39	81.05	85.01	94.80	9	85.42	83.84
11	90.92	99.57	10	90.94	89.39	94.07	103.71	10	94.43	92.46
12	99.56	108.08	11	99.57	97.45	102.92	112.53	11	103.32	100.93
13	108.24	116.59	12	108.16	106.17	111.73	121.39	12	112.13	109.15
14	117.01	125.12	13	116.80	114.49	120.72	130.27	13	121.05	118.17
15	125.11	133.64	14	125.11	122.76	129.74	138.69	14	130.00	127.01
16	133.53	141.74	15	133.58	130.91	138.03	147.56	15	138.36	135.32
17	141.98	150.20	16	141.85	139.28	146.71	156.23	16	147.13	143.69
18	150.28	158.69	17	150.24	147.40	155.52	164.71	17	155.87	152.38
19	158.68	166.92	18	158.68	155.37	164.14	173.45	18	164.42	160.67
20	166.96	175.24	19	166.94	163.69	172.67	181.91	19	173.06	168.88
21	175.29	183.49	20	175.26	171.40	181.05	190.41	20	181.48	177.35
22	183.46	191.49	21	183.47	179.31	189.72	198.89	21	190.07	185.25
23	191.70	199.62	22	191.59	187.50	198.16	207.03	22	198.52	193.33
24	199.65	207.62	23	199.63	195.14	206.50	215.35	23	206.76	201.76
25	207.68	215.57	24	207.65	202.99	214.61	223.61	24	214.98	209.53
26	215.66	223.39	25	215.61		222.87	231.64	25	223.24	217.39
27	223.58	231.05	26	223.48		231.01	239.58	26	231.33	
28	231.40	238.85	27	231.22		239.03	247.40	27	239.30	
29	239.20	246.53	28	239.02		247.25	255.34	28	247.31	
30	246.86	254.09	29	246.70		254.98	263.13	29	255.16	
31	254.10	261.60	30	254.09		262.57	270.76	30	262.85	
32	261.52	269.04	31	261.56		270.11	278.45	31	270.43	
33	269.01	276.36	32	269.02		277.60	285.72	32	278.02	
34	276.19	283.15	33	276.27		285.17	293.24	33	285.44	
35	283.23	290.45	34	283.19		292.41	300.38	34	292.82	
36	290.42	297.35	35	290.43		299.58	307.48	35	299.98	
37	297.48	304.19	36	297.41		306.76	314.29	36	307.12	
38	304.43	311.11	37	304.31		313.80	321.24	37	314.05	
39	310.96	317.96	38	311.03		320.89	328.27	38	321.06	
40	317.86		39	317.91		327.40	334.98	39	327.83	

It is known from the fact that the spin doubling in this lower state is very small that there is but slight interaction with any other electronic state of the molecule. We may consider therefore that the B_e'' values computed in the usual fashion are correct. The ratio of the two B_e'' values, which with the usual assumption of the equality of the potential energy function for the two isotopic molecules should equal ρ^2, is 0.51337. This means a decrease in the equilibrium distance between the two nuclei in CaD of 0.059 percent. Holst and Hulthén[5] have reported about the same decrease, 0.056 percent, in the distance between the two nuclei for AlD as compared to AlH in their lowest $^1\Sigma$ state.

Now Kronig has recently shown[2] that the correct treatment of the wave equations for the diatomic molecule leads to the conclusion that the potential energy curves for two isotopic molecules need not be identical provided that the "united atom" (a concept valid only for hydrides) has an $L>0$ and has other near-lying perturbing electronic states. Since the united atoms for both AlH and CaH have $L=2$ (the lowest ^2D level of Sc for CaH) and have other perturbing levels within a range of one or two volts, both molecules might be expected to show sizable and about equal decreases in equilibrium distance for their deutrides.

That the ordinary rotational energy term formula applied to the excited state of these bands does not yield correct B_v values is shown by the fact that the B_e values so obtained ($B_e'=4.4918$ for CaH and 2.2813 for CaD) have a ratio 0.50788. The explanation of this large departure in the wrong direction from the reduced mass ratio lies in the fact that the analysis of the data always gives B^* values,[3] differing from the true B_v values by terms arising from the interaction with certain other states of the molecule. If the interaction of this $^2\Sigma$ state is solely with a neighboring $^2\Pi$ state, then it may be shown that

$$B^*-B_v=-2B_v^2l(l+1)/\nu(\Pi,\ \Sigma).$$

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[5] W. Holst and E. Hulthén, Nature **133**, 496 (1934).

The interaction for this $^2\Sigma$ state of CaH being largely with the $A\ ^2\Pi$ state lying but 1320 cm^{-1} $(=\nu(\Pi, \Sigma))$ below it, this correction to B_0^* for CaH is about -0.067, while for CaD the correction is but -0.017 because of the B_v^2 factor. Inclusion of these corrections gives an indicated B_e ratio considerably nearer[6] the value ρ^2. But since interacting electronic states such as these never stand exactly in the relation of "pure precession" to each other, these corrections to obtain true B_v and B_e values can never be made with great accuracy.

The α constants for the ground state listed in Table III have a ratio almost exactly ρ^3, as they should have according to the theory of the isotope effect. Comparison of the spin doubling $\Delta\nu_{12}(K)$ in the $B\ ^2\Sigma$ state of the two isotopes is also of some interest. The variation of this doubling with K is presented in Fig. 2. Now according to theory this variation should be strictly proportional to $(K+\frac{1}{2})$, and the factor of proportionality γ should equal, if strong interaction exists between the two states, the slope p of the Λ-doubling curve for the near $^2\Pi_d$ levels. There should be a ratio B_0 between these constants for the two isotopic molecules. The expected linear spin-doubling relation does hold for CaD, the slope of the line in Fig. 2 being -0.364. Division of this by ρ^2 gives -0.709 which is nearly the value -0.704 of p for the $^2\Pi$ state of CaH. The spin-doubling curve for the CaH state shown in Fig. 2 has an initial slope of -0.945, changing for the higher rotational levels to -0.543. This change of slope is probably due to a perturbation by other near-lying rotational levels, the absence of it for CaD being attributed to the different spacing of the rotational levels. The conclusion from this comparison of B_e, B_v^* and α values, as well as the spin- and Λ-doublings, in corresponding states of these two molecules is, then, that the variation of the theoretical relations as a function of the mass of the molecule is entirely verified.

TABLE III. *Rotational constants of the "B" $^2\Sigma\rightarrow{}^2\Sigma$ CaD and CaH bands.*

	CaD	CaH		CaD	CaH
B_0''	2.1777	4.2296	$B_0'^*$	2.2600	4.4338
B_1''	2.143	4.1333	$B_1'^*$	2.215	4.318
α''	0.035	0.096	α'	0.045	0.116
B_e''	2.196	4.2776	D_0'	-5.4×10^{-5}	-2.36×10^{-4}
D_0''	-4.8×10^{-5}	-1.84×10^{-4}	D_1'	-6.5×10^{-5}	-2.44×10^{-4}
D_1''	-6.1×10^{-5}	-1.82×10^{-4}	γ'	-0.364	$\left\{\begin{array}{l}-0.945 \text{ or}\\-0.543\end{array}\right.$
γ''	0.032	0.045			

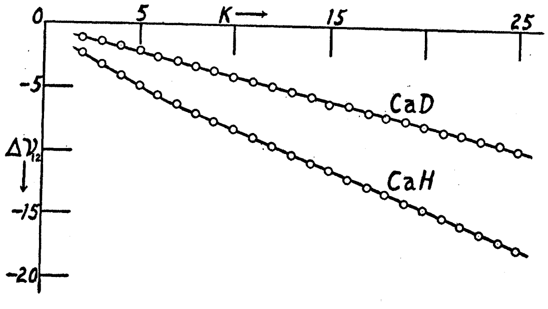

FIG. 2. Comparison of the spin doubling in the $B\ ^2\Sigma$ state of the CaD and CaH molecules.

THE *C* BANDS OF CaD

In contrast to the lack of the CaH perturbation in the $B\ ^2\Sigma$ state as mentioned above, the C band of CaD at 3534A displays violent perturbations

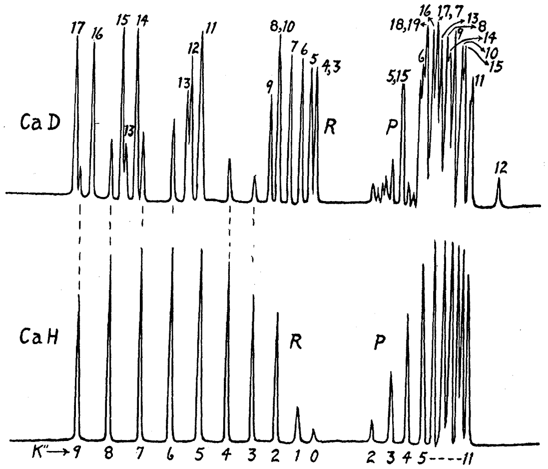

FIG. 3. Microphotometer traces of the C bands of CaD and CaH. The numbers on the CaD lines are the assigned values of K''.

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[6] It follows from the definition of q on p. 89 and of B^* in Eq. (16) of reference 3 that $B^*-B_v=-q$, not $+q$ as stated by Mulliken and Christy after their Eq. (19). Since q is in this case negative, for CaH $B_0'=4.4338-0.067=4.367$, while for CaD $B_0'=2.260-0.017=2.243$. Addition of $\frac{1}{2}\alpha$ to these quantities (using the α' values from Table IV) gives $B_e'=4.425$ and 2.265 for CaH and CaD, respectively. The ratio of these is 0.511865, fairly close to the value for ρ^2. However, the only significance to be attached to this calculation is that it forms an approximate check on these theoretical relations between B^* and B_v values.

TABLE IV. *Assignment of frequencies in the "C" $^2\Sigma\rightarrow{}^2\Sigma$ 0,0 band of CaD. cm^{-1} units.*

Int.	ν obs.	$R(K'')$	Int.	ν obs.	$P(K'')$	Unassigned
7	28469.62	$R(17)$	5	28321.73	5,15	28334.74(1) $R(1)$?
7	61.89	16	6	12.91	6	31.94(1)
8	48.66	15	9	11.28	18,19	30.40(1)
2	46.65	13	8	08.62	16	29.14(1) $R(0)$?
8	42.13	14	10	06.67	17,7	16.33(1b) $P(2)$?
4	19.18	13	7	04.68	13	14.12(5) $P(3)$?
6	17.41	12	7	02.30	8	
7	12.92	11	6b	00.89	14	
5	381.28	9	9	298.73	9	
8	77.61	8,10	7	95.45	10	
7	72.44	7	7	94.04	15	
7	67.33	6	6	90.53	11	
6	63.05	5	2	78.17	12	
6	60.81	4,3				

in its upper state which do not occur in the corresponding CaH levels. Comparison of the structure of this band for the two molecules in the reproduction in Fig. 1 and in the microphotometer traces in Fig. 3 indicates these perturbations at once. The intensities, frequencies and quantum assignments of the lines in this 0,0 C band of CaD are given in Table IV. These assignments are made with the necessary condition that there should be the same lower state $R(J-1)-P(J+1)$ combination differences as found in the B band of CaD. For these two systems have a common ground state, and no perturbations are found in this B band. Without this condition as a guide it would be quite impossible to make the quantum analysis, for every line in the band is perturbed, the resulting confusion in the P-branch being particularly bad.

A prominent feature is the sudden cessation of lines at a particular value of K, just as for the CaH band as developed in a low pressure arc.[7] The cut-off is practically at the same energy content in the upper $^2\Sigma$ state for each molecule, since the band origins lie within a few cm^{-1} of each other. An explanation of this sudden drop of the intensity to zero in the two branches as due to predissociation into the continuum of the D state of CaH has been given by Grundström and Hulthén.[8]

As usual in the phenomenon of perturbations, two lines having the same K values sometimes appear at a perturbation point. This occurs definitely at $K=14$. Also these perturbations are multiple, with centers at about $K=3$, 10, 13, and >17. This would indicate the presence in this energy range of CaD levels of more than one other state with levels spaced similarly and having all of the properties necessary for perturbing the C $^2\Sigma$ levels. The D $^2\Sigma$ state may be one of these, but of other states in this interval nothing is known. The displacements in these perturbations are evidently of the usual "anomalous dispersion curve" type, but it is difficult to calculate the exact magnitudes of the shifts because of the fact that there are no unperturbed lines from which the normal course of the levels may be computed. From an attempt at such a calculation, by using predicted constants from the isotope effect theory, it is evident that, as for the C state of CaH, a sizable term linear in K is present and with a coefficient about in the ratio ρ^2 to the 2.22 value[8] for CaH. Finally, it should be mentioned that the 0,1 band of this CaD system is also present on our spectrograms, but with rather low intensity. Inspection shows that large perturbations similar to those of the 0,0 band occur in its branches. The same perturbations should be found in the two bands, of course, because of their common upper state.

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[7] R. S. Mulliken, Phys. Rev. **25**, 509 (1925).

[8] Cf. B. Grundström, Zeits. f. Physik **69**, 235 (1931).

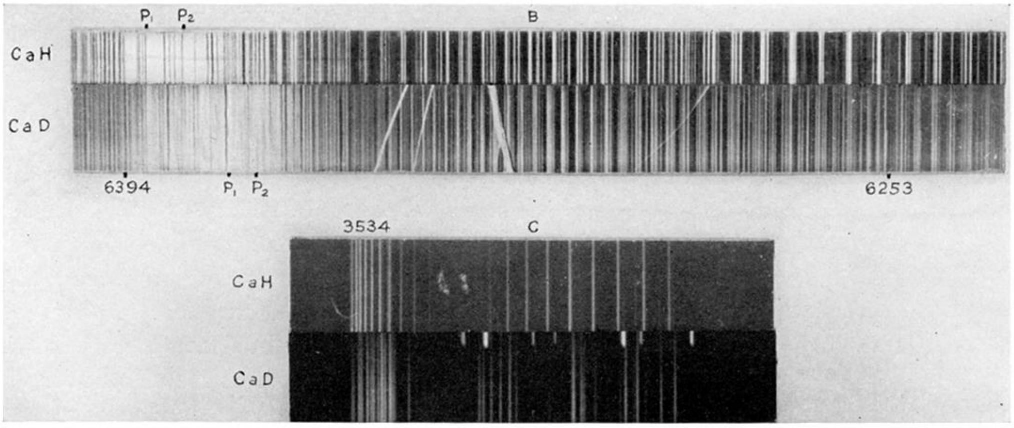

FIG. 1. Spectrograms of the *B* and *C* bands of CaH and CaD. Both of the CaD spectra have the CaH bands present with low intensity, and the spectrogram of the CaH *C* band shows some of the CaD lines. Note the marked difference between the *C* bands of the two isotopes.